



Impact of dust deposition on carbon budget: a tentative assessment from a mesocosm approach

Cécile Guieu, Céline Ridame, Elvira Pulido-Villena, Matthieu Bressac, Karine Desboeufs, François Dulac

► To cite this version:

Cécile Guieu, Céline Ridame, Elvira Pulido-Villena, Matthieu Bressac, Karine Desboeufs, et al.. Impact of dust deposition on carbon budget: a tentative assessment from a mesocosm approach. *Bio-geosciences*, 2014, 11 (19), pp.5621-5635. 10.5194/bg-11-5621-2014 . hal-01139588

HAL Id: hal-01139588

<https://hal.science/hal-01139588>

Submitted on 9 Dec 2015

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons Attribution| 4.0 International License



Impact of dust deposition on carbon budget: a tentative assessment from a mesocosm approach

C. Guieu^{1,2}, C. Ridame^{3,4}, E. Pulido-Villena⁵, M. Bressac^{1,2,*}, K. Desboeufs⁶, and F. Dulac⁷

¹Sorbonne Universités, UPMC Univ. Paris 06, UMR 7093, LOV, Observatoire océanologique, 06230 Villefranche/mer, France

²CNRS, UMR 7093, LOV, Observatoire océanologique, 06230 Villefranche/mer, France

³CNRS-INSU/IRD/ MNHN/UPMC, UMR 7159, LOCEAN, Laboratoire d'Océanographie et du Climat: Expérimentation et Approches Numériques, 75252 Paris, France

⁴Sorbonne Universités, UPMC Univ Paris 06, UMR 7159, LOCEAN, 75252 Paris, France

⁵Aix Marseille Université, CNRS/INSU, IRD, Mediterranean Institute of Oceanography (MIO), UM 110, 13288 Marseille, France

⁶Université Paris Diderot, Sorbonne Paris Cité, Université Paris Est Créteil, UMR CNRS 7583, Laboratoire Interuniversitaire des Systèmes Atmosphériques (LISA), 61 av. Gal de Gaulle, 94010 C, France

⁷Laboratoire des Sciences du Climat et de l'Environnement (LSCE), UMR 8212 CEA-CNRS-UVSQ, 91191 Gif-Sur-Yvette, France

*University of Tasmania, Institute for Marine and Antarctic Studies (IMAS), Hobart, Tasmania, Australia

Correspondence to: C. Guieu (guieu@obs-vlfr.fr)

Received: 7 January 2014 – Published in Biogeosciences Discuss.: 29 January 2014

Revised: 3 September 2014 – Accepted: 9 September 2014 – Published: 14 October 2014

Abstract. By bringing new nutrients and particles to the surface ocean, atmospheric deposition impacts biogeochemical cycles. The extent to which those changes are modifying the carbon balance in oligotrophic environments such as the Mediterranean Sea that receives important Saharan dust fluxes is unknown. The DUNE (DUSt experiment in a low Nutrient, low chlorophyll Ecosystem) project provides the first attempt to evaluate the changes induced in the carbon budget of a large body of oligotrophic waters after simulated Saharan dust wet or dry deposition events, allowing us to measure (1) the metabolic fluxes while the particles are sinking and (2) the particulate organic carbon export. Here we report the results for the three distinct artificial dust seeding experiments simulating wet or dry atmospheric deposition onto large mesocosms (52 m³) that were conducted in the oligotrophic waters of the Mediterranean Sea in the summers of 2008 and 2010. Although heterotrophic bacteria were found to be the key players in the response to dust deposition, net primary production increased about twice in case of simulated wet deposition (that includes anthropogenic nitrogen). The dust deposition did not produce a shift in the metabolic

balance as the tested waters remained net heterotrophic (i.e., net primary production to bacteria respiration ratio < 1) and in some cases the net heterotrophy was even enhanced by the dust deposition. The change induced by the dust addition on the total organic carbon pool inside the mesocosm over the 7 days of the experiments, was a carbon loss dominated by bacteria respiration that was at least 5–10 times higher than any other term involved in the budget. This loss of organic carbon from the system in all the experiments was particularly marked after the simulation of wet deposition. Changes in biomass were mostly due to an increase in phytoplankton biomass but when considering the whole particulate organic carbon pool it was dominated by the organic carbon aggregated to the lithogenic particles still in suspension in the mesocosm at the end of the experiment. Assuming that the budget is balanced, the dissolved organic carbon (DOC) pool was estimated by the difference between the total organic carbon and the particulate organic carbon (POC) pool. The partitioning between dissolved and particulate organic carbon was dominated by the dissolved pool with a DOC consumption over 7 days of $\sim 1 \mu\text{mol C L}^{-1} \text{ d}^{-1}$ (dry

deposition) to $\sim 2\text{--}5\ \mu\text{mol C L}^{-1}\text{ d}^{-1}$ (wet deposition). This consumption in the absence of any allochthonous inputs in the closed mesocosms meant a small $< 10\%$ decrease of the initial DOC stock after a dry deposition but a $\sim 30\text{--}40\%$ decrease of the initial DOC stock after wet deposition. After wet deposition, the tested waters, although dominated by heterotrophy, were still maintaining a net export (corrected from controls) of particulate organic carbon (0.5 g in 7 days) even in the absence of allochthonous carbon inputs. This tentative assessment of the changes in carbon budget induced by a strong dust deposition indicates that wet deposition by bringing new nutrients has higher impact than dry deposition in oligotrophic environments. In the western Mediterranean Sea, the mineral dust deposition is dominated by wet deposition and one perspective of this work is to extrapolate our numbers to time series of deposition during similar oligotrophic conditions to evaluate the overall impact on the carbon budget at the event and seasonal scale in the surface waters of the northwestern Mediterranean Sea. These estimated carbon budgets are also highlighting the key processes (i.e., bacterial respiration) that need to be considered for an integration of atmospheric deposition in marine biogeochemical modeling.

1 Introduction

Atmospheric deposition provides new nutrients to the marine environment and, in a number of oligotrophic environments submitted to significant deposition, those new nutrients are likely able to relieve ongoing (co)limitations by providing nitrogen, phosphorus, iron and other micronutrients (de Leeuw et al., 2013) available both for phytoplankton and heterotrophic bacteria. Depending on the balance between the autotrophic vs. heterotrophic community, the stimulation by atmospheric deposition may thus either result in a CO_2 input or a CO_2 output. Such opposite effects in terms of carbon (C) fate deserve to be explored if we want to understand the role of atmospheric deposition in marine ecosystem functioning, C cycling and feedbacks on climate. Biological responses to natural, polluted or mixed aerosols inputs have been explored in a number of experimental artificial aerosols additions and in situ observations. In a recent paper, Guieu et al. (2014a) have synthesized the results from 26 of those studies showing that biota in low-nutrient and low-chlorophyll (LNL) areas positively responds to aerosol addition, with bacterial production and N_2 fixation showing the strongest responses. Increases in chlorophyll *a* (Chl *a*) have also been seen but to a lesser extent. This synthesis shows that changes in biological standing stocks tend to be smaller than changes in metabolic rates (i.e., Chl *a* vs. primary production and bacterial abundance vs. bacterial respiration and/or production). As previously reported, this could be due to the effect of grazing by zooplankton on phytoplank-

ton and bacteria (e.g., Bonnet et al., 2005; Herut et al., 2005; Marañón et al., 2010) which may increase turnover at the expense of stocks and rapidly propagate responses through the whole food web. The use of metabolic rates instead of stocks seems more appropriate in tackling the response of biota to atmospheric deposition. Few studies have so far considered together the changes in metabolic rates induced by atmospheric deposition for both autotrophic and heterotrophic communities: Herut et al. (2005) showed that both communities were highly stimulated after fresh dust addition to surface seawater in microcosm experiments with bacterial production (BP) stimulated twice as much as primary production (PP) in the ultraoligotrophic eastern Mediterranean Sea (increase of 770 and 450 %, respectively). Marañón et al. (2010) conducted eight bioassay experiments, over the basin-wide geographical range in the tropical Atlantic and have shown that the effect of Saharan dust deposition on the biological activity of the surface ocean may vary with the degree of oligotrophy of the tested waters. For four out of the eight addition experiments, the relative change in response to dust exceeded a value of 200 % for BP and community respiration (CR), whereas PP never increased by more than 100 % (Marañón et al., 2010). In the western Mediterranean Sea, Pulido-Villena et al. (2008) also showed a strong stimulation of bacterial respiration (BR) after dust deposition either in microcosms (125 % average increase in BR) or in situ (100 % increase); the stimulation being proportional to the intensity of the dust flux. Unfortunately, no autotrophic metabolic rate was measured during that study. *In situ* increase of bacterial production and biomass in the Villefranche Bay was also shown after a major Saharan dust deposition (Bonilla-Findji et al., 2010) occurred in the northwestern Mediterranean Sea (22.2 g m^{-2} of dust were deposited in a few hours on the 21 February 2004; Ternon et al., 2010). Lekunberri et al. (2010) simulated in vitro a substantially stronger dust event (final microcosm dust concentration of $50\text{--}500\text{ mg L}^{-1}$), showing that the lower dust addition (50 mg L^{-1}) resulted in a more heterotrophic system.

Although these recent studies have shown that dust deposition can impact phytoplankton, heterotrophic bacteria and the metabolic balance, they did not take into consideration the impact on POC export. And yet, it has been shown recently that aggregation and sorption processes between atmospheric lithogenic particles and in situ (dissolved and particulate) organic matter and subsequent ballasting can induce a strong and rapid POC export independently of a fertilization effect (Ternon et al., 2010; Bressac and Guieu, 2013; Bressac et al., 2014; Desboeufs et al., 2014). A major improvement compared to previous studies would thus rely on the consideration of a dust addition that mimics the actual deposition process, allowing us to measure the metabolic fluxes while the particles are sinking and the particulate organic carbon export. As shown in Guieu et al. (2014b), the 52 m^3 mesocosm strategy developed during the DUNE (a DUst experiment in a low Nutrient, low chlorophyll Ecosys-

tem; <http://www.obs-vlfr.fr/LOV/DUNE/index.html>) project allows us to consider a number of stocks and fluxes after a representative simulation of atmospheric deposition performed in situ at the surface of a large body of water. Considering the vertical transport of particles within the 15 m depth of the mesocosms over a representative length of time (up to 7 days after the deposition) is an important improvement compared to the microcosm strategy where smaller volumes of tested waters (up to 15 L in the studies mentioned above) are kept homogenized along the course of usually very short experiments (2–6 days; Guieu et al., 2014a). In the large mesocosms, the settling of the particles through the water column and interactions with naturally occurring particles are both integrated.

Two campaigns to study the impact following different scenarios of dust deposition were conducted in the frame of project DUNE: DUNE-1 campaign in June 2008 and DUNE-2 campaign in June–July 2010. DUNE-1 consisted in two distinct 8-day experiments: a first simulation of a Saharan wet deposition event (hereafter named DUNE-P) and a second simulation of a Saharan dry deposition event (hereafter named DUNE-Q). DUNE-2 consisted of a single 16-day experiment (hereafter named DUNE-R) with two successive dust wet deposition simulations with 7 days between each seeding (respectively named DUNE-R1 and DUNE-R2). The purpose of having two campaigns (2008 and 2010) at the same period (beginning of summer) was to test different scenarios of deposition with similar in situ conditions. For that purpose, in 2008, we indeed performed two distinct experiments to investigate whether dry and wet depositions were followed by the same impacts; in 2010, we tested if two successive deposition fluxes of similar magnitude and duration result in similar impacts and, if so, what are the underlying reasons? This strategy of two successive seedings was decided following DUNE-1 results. Indeed, Wagener et al. (2010) showed that dust addition during DUNE-P was followed by a decrease of dissolved iron (DFe) concentration likely due to DFe scavenging on settling dust particles giving evidence that large dust deposition events may be a sink for surface ocean dissolved iron. Combining the mesocosm experiment with a batch dissolution experiment, Wagener and collaborators have then shown that following dust addition, biological activity was enhanced and Fe-binding ligands were produced, then DFe increased. Although two successive deposition events of this intensity have not been reported, to our knowledge, this strategy was thus planned in order to explore how dust deposition does impact biogeochemistry under different in situ, biogeochemical initial conditions.

Here we report PP, BR and particulate organic carbon export ($\text{POC}_{\text{export}}$) data acquired during DUNE-P, -Q and -R experiments. All the PP data are from Ridame et al. (2014); BR for DUNE-P and -Q are original data whereas BR data from DUNE-R are from Pulido-Villena et al. (2014a). $\text{POC}_{\text{export}}$ data from trap measurements are from companion pa-

pers (DUNE-P, -Q and -R in Desboeufs et al., 2014, and DUNE-R in Bressac et al., 2014). First we explore how the balance between bacterial respiration and net primary production is altered following the dust deposition. Then, we attempt to use the numbers measured (stocks and fluxes), along with estimates, to examine how the carbon budget, likely modified by the introduction of dust, can be balanced.

2 Methods

2.1 Mesocosm approach

The methodology developed during project DUNE for (1) the production of dust analogs to simulate wet and dry dust deposition events and (2) the artificial seeding over large clean mesocosms allowing us to follow and quantify the chemical and biological changes, along with modifications of the dynamics of particles following a dust deposition is fully described in Guieu et al. (2010, 2014b); and the two field campaigns, the results of which are reported here, are described in a companion paper (Guieu et al., 2014b). Only a short summary is given in this section. The mesocosms setup, the ways the dust was seeded and the sampling inside the mesocosms can be seen here (see video in Supplement).

2.1.1 Study site

The two DUNE campaigns were conducted in a remote, coastal, LNLC area of the Mediterranean Sea: the Scandola preservation area located in the island of Corsica. It is a marine and terrestrial zone protected from human activities since its creation in 1975. The selected site (Elbo Bay) has a seafloor at ~ 30 m depth covered by sand and seagrass. There is no terrestrial access, and several restrictions are imposed upon boat activities (e.g., no mooring allowed during nighttime). The closest town is a small village located at 5.88 miles (11 km), and there is no industrial activity in the region. There are no nearby rivers, and the site can only be influenced by direct runoff from the land.

2.1.2 Mesocosm setup

The mesocosms consisted of large bags made of two 500 μm thick films of polyethylene mixed with vinyl acetate (EVA; 19 %) with nylon meshing in between to allow maximum resistance and light penetration (produced by HAIKONENE KY, Finland). They were 2.3 m in diameter at the surface and 15 m in height with an emerging portion of ~ 70 cm. At the base of the mesocosm, a very simple sediment trap system allowed the divers to rapidly change the traps. All the material used for the installation was made with plastic, including the structures holding the bags and on which the mooring was attached. In order to exclude the possibility that a “real” deposition event could disturb the experiment, the mesocosms were covered with transparent PVC

(polyvinyl chloride) material. These covers were elevated to 10 cm above the top of the mesocosms, allowing air to circulate in order to avoid a confinement effect in the trapped water. Indeed, the comparison of the temperature measured continuously inside and outside the mesocosm showed that temperature inside the mesocosms was at maximum 3 % higher and 2 % lower than outside (Fig. 6 in Guieu et al., 2014b). The structures were moored using only nonmetallic material (except for the screw anchors installed at the sea floor 25–30 m deep). The strategy consisted in the deployment of one group of three mesocosms CONTROL (no dust addition, named hereafter CONTROL-MESO) and one group of three mesocosms DUST (each with dust addition corresponding to a dust flux of 10 g m^{-2} , see details below, named hereafter DUST-MESO).

2.1.3 Simulation of mineral dust deposition

The dust deposition was mimicked using the finest fraction ($< 20 \mu\text{m}$) of alluvial soils collected in a desert soil source area in south Tunisia known to export aeolian dust to the western Mediterranean (Guieu et al., 2010). Dry deposition was mimicked using the raw soil dispersed in surface seawater whereas wet deposition was mimicked using the same sieved soils after a chemical treatment reproducing cloud water processing by condensation–evaporation, diluted in ultrapure water. The methodology to produce those proxies of wet and dry dust deposition is fully described in Guieu et al. (2010) and their respective detailed composition is reported in Desboeufs et al. (2014). Both dust types had similar chemical composition for phosphorus, carbon, and iron but not for nitrogen because of the addition of HNO_3 in the simulated cloud water used to process dust for wet deposition simulation (Guieu et al., 2010).

2.1.4 Sampling the mesocosms

An original sampling system was designed with the goal of inducing the least possible perturbation inside the mesocosms during sampling. In each bag, three clear, braided PVC tubing (Hozelock-Tricoflex, inside diameter of 9.5 mm) were permanently installed at the center of the bags with one end at three different depths: 10, 5 and 0.1 m. The sampling was done every day at the same hour by pumping water at the different selected depths without introducing any device inside the mesocosm. In order to do this a metal free pump (Saint-Gobain Performance Plastics) activated by the pressurized air from a diving tank was connected successively to the ends of the tubing coming out of the mesocosm. In between the two groups of three mesocosms, reference measurements were performed in free seawater (OUT) using the same sampling device. The sediment traps were collected by divers every 2 days during DUNE-1 and every day during DUNE-2. In addition, temperature was continuously monitored inside and outside mesocosms.

All seeding and sampling operations in the mesocosms were performed from mobile plastic platforms that were moved using several two-way ropes installed in between buoys (see video in Supplement).

2.2 Methodology for the acquisition of the data presented in this paper

The methods for sampling and measuring PP, BR and POC export are fully described in companion papers (Ridame et al., 2014, Pulido-Villena et al., 2014a; Bressac et al., 2014, respectively). The main points are summarized here.

2.2.1 PP

Samples were collected at both 0.1 and 5 m depths during DUNE-P and -Q experiments and at 5 m depth during DUNE-R experiment, for the determination of PP using the ^{13}C uptake determination method. Immediately after sampling, ^{13}C tracer was added to obtain a final enrichment of about 9 at. % excess. Then, the ^{13}C -amended bottles were incubated under in situ conditions on a mooring line for 24 h at the corresponding sampling depths. Incubations were ended by filtration onto precombusted 25 mm glass fiber filters. Sample filters were stored at -20°C and dried at 40°C for 48 h before analysis. Concentration of carbon in particulate matter and ^{13}C enrichment were quantified using a ThermoFisher ScientificTM (Bremen, Germany) isotope ratio mass spectrometer (IRMS) Delta plus, coupled with a C/N analyzer Flash EA via a type III interface. This primary production could be considered as the net particulate primary production. Based on (1) the significant similarity ($p > 0.05$) of the Chl *a* concentrations measured at 0.1, 5 and 10 m depths in the three experiments and (2) the comparable results ($\pm 4\%$) found for depth-integrated PP taking into account PP measured at 0.1 and 5 or 0.1, 5 and 10 m (DUNE-1) and measured at 5 or 0.1, 5 and 10 m (DUNE-2) on selected sampling days (see details in Ridame et al., 2014), the depth-integrated fluxes of PP were estimated assuming that the measurements at 0.1 and 5 m (DUNE-1) and at 5 m (DUNE-2) were representative of the flux over the entire mesocosm (Ridame et al., 2014).

2.2.2 BR

Briefly, 5 m depth samples from each mesocosm were collected, gently filtered through a $0.8 \mu\text{m}$ polycarbonate filter under low vacuum pressure and siphoned into a set of six biological oxygen demand (BOD) bottles. Three BOD bottles from each mesocosm were immediately fixed with Winkler reagents. The other three were incubated during 24 h in the dark in a tap water bath to minimize temperature variations and were then fixed with Winkler reagents. Oxygen concentration was measured through a spectrophotometric approach based on measuring the absorbance at 466 nm of the colored I_2 and I_3^- (Labasque et al., 2004; Reinthaler et

al., 2006). Calibrations were performed daily between 200 and 250 $\mu\text{mol O}_2 \text{ L}^{-1}$ using a KIO_3 standard. The regression between O_2 concentration and absorbance at 466 nm was performed using standard software to obtain the slope. The intercept corresponded to the reagent blank and averaged 0.25 $\mu\text{mol O}_2 \text{ L}^{-1}$. The detection limit was 0.4 $\mu\text{mol O}_2 \text{ L}^{-1}$. There is recent evidence that the in vitro O_2 bottle incubation technique used, involving prefiltration and long incubation time, could lead to an overestimation of the BR rates (see, for example, Aranguren-Gassis et al., 2012). This controversy about the methods used and how this could have important consequences on our view of ocean autotrophy vs. heterotrophy functioning has recently been the subject of several articles (Ducklow and Doney, 2013; Duarte et al., 2013; Williams et al., 2013) showing that there is no consensus so far. This potential overestimation should not be a big problem as far as results are compared with literature data (obtained with the same method) and/or relative changes after dust addition are concerned.

To convert oxygen consumption to carbon respiration, a respiratory quotient of 1 was assumed (Del Giorgio and Cole, 1998). Based on the homogeneity of bacteria abundance for DUNE-P, -Q and -R (E. Pulido-Villena, personal communication, 2014b), the fluxes were integrated over the mesocosm depth assuming that the measurement at 5 m is representative of the flux over the mesocosm. Heterotrophic bacteria have been shown to be uniformly distributed with depth within the euphotic zone, usually corresponding to the layer between the surface and the deep chlorophyll maximum (Tanaka et al. 2002). Therefore, within the 15 m depth surface layer enclosed by the mesocosms, little variations in bacterial activity may be expected.

2.2.3 $\text{POC}_{\text{export}}$

Samples from sediment traps located ~ 14.3 m above the surface of the mesocosms were preserved using a 5 % buffered solution of formaldehyde. Swimmers were carefully hand-picked and the remaining sample was desalted using ultrapure water and freeze-dried. Mass flux was determined by weighing the entire freeze-dried sample. The total concentration of carbon (TC) was measured using a CHN analyzer (Perkin Elmer 2400). HNO_3/HF acid-digestion was performed in 7 mL Teflon flasks at 150 °C. Following complete evaporation, samples were diluted in 0.1 M HNO_3 and analyzed for their calcium (Ca), and sulfur (S) concentrations by ICP-AES (inductively coupled plasma atomic emission spectrometry; Desboeufs et al., 2014). In dust analogs, Ca is present both as calcium carbonate and calcium sulfate (Guieu et al., 2010; Desboeufs et al., 2014). The part of Ca associated with sulfate ($\%\text{CaCaSO}_4$) was estimated from the particulate S concentration. Therefore, the particulate Ca concentration as carbonate ($\%\text{CaCaCO}_3$) corresponded to the difference between total Ca ($\%\text{Ca}$) and $\%\text{CaCaSO}_4$. The carbonate fraction (CaCO_3) was determined from

the $\%\text{CaCaCO}_3$ ($\%\text{CaCO}_3 = 100/40 \times \%\text{CaCaCO}_3$). Particulate inorganic carbon (PIC) was then deduced from CaCO_3 ($\%\text{PIC} = 12/100 \times \%\text{CaCO}_3$). Finally, $\text{POC}_{\text{export}}$ was determined by subtracting PIC from TC in sediment trap samples. The whole data set is presented in Supplement Table S1.

2.3 Statistical test

In order to compare the results between experiments, RC (relative changes) were compared using a one-way ANOVA (analysis of variance) and a Fisher least significant difference (LSD) means comparison test ($\alpha = 0.05$). When assumptions for ANOVA were not respected, means were compared using a Kruskal–Wallis test and a post hoc Dunn's test. The statistical tests and the box plots were performed using the Addinsoft XLSTAT software (<http://www.xlstat.com>).

2.4 Calculation of the different terms of the carbon balance

The changes in the carbon pool induced by the seeding during 7 days inside the DUST-MESO as compared to the CONTROL-MESO involve different terms corresponding to organic carbon addition and loss. This can be written as follows:

$$\begin{aligned} (\delta C_{\text{org}}/\delta t) &= (\delta \text{POC}/\delta t) + (\delta \text{DOC}/\delta t) \\ &= (\delta \text{NCP}/\delta t) - (\delta \text{POC}_{\text{export}}/\delta t) + \text{At}_{\text{input}}, \end{aligned} \quad (1)$$

where NCP is the net community production, $\text{POC}_{\text{export}}$ the particulate organic carbon exported downward as measured in the sediment traps, and At_{input} the amount of organic carbon added by the top to the DUST-MESO by seeding (0.31 % of the total dust as determined by Desboeufs et al., 2014). NCP is the difference between gross primary production (GPP) and community respiration (that comprise BR, zooplankton respiration (ZR) and autotroph respiration (AR)). As net particulate PP (measured in this study) plus dissolved primary production (DPP) is equal to the difference between GPP and respiration of the autotrophs, the equation can be written as follows:

$$\begin{aligned} (\delta C_{\text{org}}/\delta t) &= (\delta \text{POC}/\delta t) + (\delta \text{DOC}/\delta t) \\ &= (\delta \text{PP}/\delta t) + \delta \text{DPP}/\delta t + (\delta \text{AR}/\delta t) - (\delta \text{BR}/\delta t) \\ &\quad - (\delta \text{AR}/\delta t) - (\delta \text{ZR}/\delta t) - (\delta \text{POC}_{\text{export}}/\delta t) + \text{At}_{\text{input}} \\ &= (\delta \text{PP}/\delta t) + (\delta \text{DPP}/\delta t) - (\delta \text{BR}/\delta t) - (\delta \text{ZR}/\delta t) \\ &\quad - (\delta \text{POC}_{\text{export}}/\delta t) + \text{At}_{\text{input}}. \end{aligned} \quad (2)$$

As reported by Mara  n et al. (2005) and references within, “all the evidence suggests that the release of recent photosynthate in dissolved form accounts for a substantial fraction of total primary production in oligotrophic ecosystems”. As a matter of fact, this fraction was found to be on average 12 % from a statistical study on marine-estuarine systems (Baines and Pace, 1991), 22 % in situ for open ocean

oligotrophic systems (i.e. Mara  n et al., 2005), and 19 % from a mesocosm study in a coastal productive ecosystem (L  pez-Sandoval et al., 2010). More specifically in the open Mediterranean Sea, L  pez-Sandoval et al. (2011) during the BOUM (Biogeochemistry from the Oligotrophic to the Ultra-oligotrophic Mediterranean) cruise in summer reported that dissolved primary production remained quite constant and represented 37 % of total primary production along the longitudinal gradient. In the absence of direct measurement of DPP during the DUNE experiments, we will use the average number calculated from a robust recent data set and replace the term DPP in Eq. (2) by $DPP = 0.37 \times (PP + DPP) = 0.59 \times PP$. The contribution of the mesozooplankton respiration to total primary production has been estimated from a number of studies conducted in June–July (Alcaraz, 1988; Calbet et al., 1996; Alcaraz et al., 2007) in the northwestern Mediterranean Sea and a range 13–27 % of PP has been assumed in the absence of direct measurement of zooplankton respiration during the DUNE experiments.

Finally, to calculate the changes induced by the seeding inside the mesocosm in the particulate carbon pool ($\delta POC / \delta t$), we have to consider the sum of two terms: (term 1) the changes in the organic carbon pool of phytoplankton, micro- and mesozooplankton, and bacteria plus (term 2) a fraction of POC associated with added lithogenic material (POC_{dust}) (Bressac et al., 2012, 2014) and still in suspension inside the mesocosm at the end of the experiment (Desboeufs et al., 2014).

For term 1, the organic carbon pools of phytoplankton were deducted from Chl *a* concentration (Guieu et al., 2014b) with a conversion factor $C / Chl\ a\ (w : w) = 103$ for cells $< 2\ \mu m$ and $C / Chl\ a = 247$ for cells $> 2\ \mu m$ (from P  rez et al., 2006) in the Atlantic subtropical gyre, an oligotrophic environment dominated by picoplankton, which has similar conditions as during DUNE (Giovanetti et al., 2013). The discrimination between size cells is based on Giovanetti et al. (2013), who report that Chl *a* in the $< 3\ \mu m$ fraction represents 70 % of the total Chl *a* during the DUNE-R experiment. The organic carbon pool of microzooplankton was deduced from the abundance of heterotrophic nanoflagellates (HNFA) that was determined at 5 m depth during the DUNE-R experiment. As no significant difference between CONTROL-MESO and DUST-MESO at any of the seeding periods was reported by Pulido-Villena et al. (2014a), we conclude that the HNFA did not contribute to any significant change in the particulate organic carbon pool after the seeding. This conclusion was extrapolated to DUNE-P and DUNE-Q as no data were available for HNFA of those experiments. The organic carbon pool of macrozooplankton was deduced from the biovolume of mesozooplankton with size $> 200\ \mu m$ that has been analyzed using a zooscan system (L. Stemmann, personal communication, 2012, and the RADEZOO service, OOV Villefranche-sur-Mer) from net sampling performed at the beginning of ex-

periments outside the mesocosms and both inside and outside after the last sampling of the DUNE-P, -Q and -R experiments. When a difference in biovolume was found between DUST-MESO and CONTROL-MESO (DUNE-P experiment), a ratio of biovolume to zooplankton carbon equal to $\sim 0.03\ mg\ C\ mm^{-3}$ (Calbet et al., 1996) was used to calculate the increase in zooplankton biomass. Finally, the organic carbon pool of heterotrophic bacteria was deduced from their abundance which was measured from samples collected at 0.1, 5 and 10 m (P, Q: E Pulido-Villena, personal communication, 2014b; R: Pulido-Villena et al., 2014). When a difference in bacteria abundance was found between DUST-MESO and CONTROL-MESO, a factor of $12.4\ fg\ C\ cell^{-1}$ (Fukuda et al., 1998) was applied to determine the corresponding increase in biomass.

For the term 2, the strong correlation between lithogenic and POC fluxes, found in the sediment traps of the DUST-MESO over the course of all the experiments after the seeding (Bressac et al., 2014; Desboeufs et al., 2014), was used to deduce the POC fraction associated to the remaining lithogenic pool (POC_{dust}) and still in suspension in the mesocosm at the end of the experiment (details of the calculation in Table S2 in the Supplement).

3 Results

3.1 Initial environmental conditions, background fluxes and pattern of the stratification

Initial in situ conditions are reported in Table 1 for all the DUNE experiments. Concentrations were quite similar in terms of Chl *a* and nutrient concentrations. During all experiments, the tested waters were typical of oligotrophic conditions with Chl *a* concentrations in the range $0.07\text{--}0.11\ \mu g\ L^{-1}$. The DOC concentration, measured only at the beginning of DUNE-P was $87 \pm 9\ \mu M$. PP fluxes at the beginning of the three experiments were very similar, in the range $49\text{--}60\ mg\ C\ m^{-2}\ d^{-1}$. Initial BR fluxes measured for DUNE-Q and DUNE-R were comparable ranging $155\text{--}188\ mg\ C\ m^{-2}\ d^{-1}$ whereas the BR initial flux was twice as much at the beginning of DUNE-P with an average value of $433\ mg\ C\ m^{-2}\ d^{-1}$. During all the DUNE experiments, the average PP/BR ratios were always ≤ 0.5 in the CONTROL-MESO (Fig. 1). A comparable initial POC_{export} in tested waters was found for DUNE-P and DUNE-Q with a range of $2.4\text{--}3.3\ mg\ C\ m^{-2}\ d^{-1}$; at the beginning of DUNE-R, fluxes were in the same order of magnitude (average $9.8\ mg\ C\ m^{-2}\ d^{-1}$).

As detailed in Guieu et al. (2014b), for DUNE-P and DUNE-R experiments, no strong and established stratification over the course of the experiment could be observed. For DUNE-Q, there was a sharp thermocline at 5 m depth attributed to a shift during DUNE-1 from spring to summer conditions between P and Q experiments.

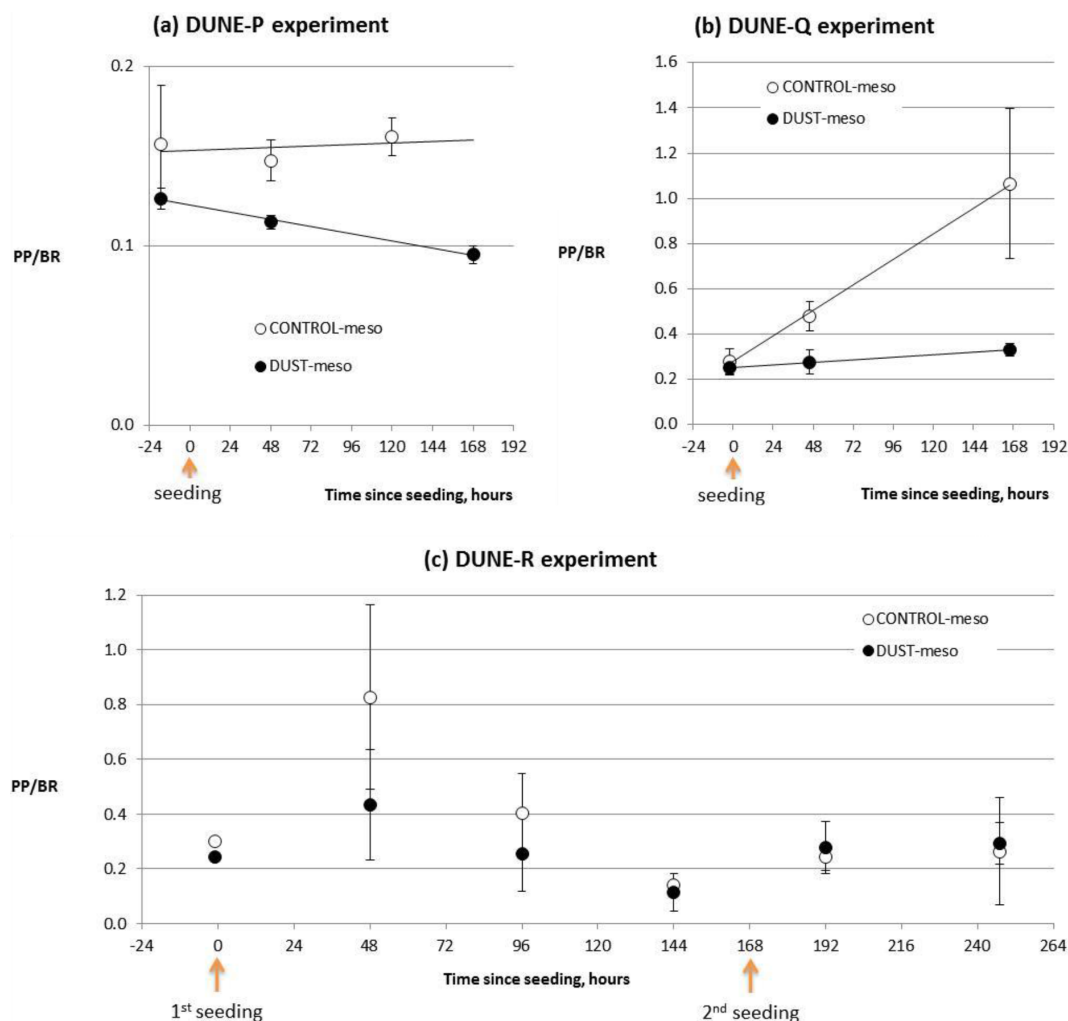


Figure 1. Evolution of the ratio PP/BR in CONTROL-MESO and after seeding in DUST-MESO (a) during DUNE-P experiment, (b) Q experiment and (c) R experiment. Vertical arrows indicate seeding time (time origin for DUNE-P, -Q, and -R1, 168 h for DUNE-R2).

3.2 Induced fluxes changes

The relative changes (RC in percentage) between DUST-MESO and CONTROL-MESO after the seeding are represented in Fig. 2. The average increases relative to CONTROL-MESO over 7 days as high as $\sim 500\%$ were observed only for $\text{POC}_{\text{export}}$. PP did not increase after seeding during the DUNE-Q experiment (dry deposition), while it increased in the range 75–144 % for the other experiments. BR increased in the range 137–156 % in DUNE-P, DUNE-Q and DUNE-R2 ; a factor 2 higher increase in BR was observed after the DUNE-R1 seeding (291 %).

PP/BR ratios were below 1 with the average value for the whole data set being 0.30 ± 0.22 . As seen in Fig. 1, PP/BR tends to be lower in DUST-MESO compared to CONTROL-MESO for DUNE-P and DUNE-Q, indicating that the dust deposition induced an increase in the net heterotrophic character of the tested waters in these experiments.

3.3 Induced changes in the carbon pools

The changes induced in the total organic carbon pool (Table 2) indicate that over the 7 days of the experiments, the dust addition resulted in a carbon loss dominated by bacteria respiration that was at least 5–10 times higher than any other term involved in the budget. This loss of organic carbon of the system in all the experiments was particularly marked after the three simulated wet deposition events (DUNE-P, DUNE-Q, DUNE-R) (Table 2). It is important to note here that although some of the terms have been estimated in the absence of direct measurements, those terms represents only a small fraction of the dominant pool represented by BR. Consequently, the errors potentially induced by these estimations have likely little impact on the final estimation of the changes induced in the organic carbon pool.

According to our calculations, the changes induced by the dust addition to the particulate organic carbon pool

Table 1. Initial conditions of the tested waters during DUNE-P, DUNE-Q and DUNE-R experiments (all depths average in the CONTROL-MESO, DUST-MESO (before seeding), and OUT).

	DUNE-1		DUNE-2
	DUNE-P	DUNE-Q	DUNE-R
Temperature	19.6 ± 0.7	20.3 ± 0.5	21.2 ± 0.4
Chl <i>a</i> , µg L ⁻¹	0.11 ± 0.03	0.08 ± 0.02	0.07 ± 0.02
NO ₃ ⁻ , nM	nd	nd	< dl ^a
DIP, nM	5 ± 2 ^b	2 ± 0 ^c	5 ± 3 ^d
DFe, nM	2.4 ± 0.3 ^e	2.3 ± 0.3 ^g	3.3 ± 0.8 ^f
DOC, µM	87 ± 9	nd	nd
PP mg C m ⁻² d ^{-1a}	60 ± 5 (<i>n</i> = 7) ^a	50 ± 5 (<i>n</i> = 7) ^a	49 ± 6 (<i>n</i> = 5) ^a
(µg CL ⁻¹ d ⁻¹)	4.8 ± 0.4	4.0 ± 0.4	3.9 ± 0.5
BR mg C m ⁻² d ⁻¹	433 ± 42 (<i>n</i> = 7)	188 ± 37 (<i>n</i> = 7)	155 ± 31 (<i>n</i> = 3) ^d
(µg CL ⁻¹ d ⁻¹)	35 ± 3	15 ± 3	12 ± 2
POC export, mg C m ⁻² d ⁻¹	3.3 ± 2.1 ^h (<i>n</i> = 3)	2.4 ± 0.9 ^h (<i>n</i> = 3)	9.8 ± 0.9 ^{h,i} (<i>n</i> = 3)

^a Ridame et al. (2014), ^b Pulido-Villena et al. (2010), ^c E. Pulido-Villena, personal communication, 2014b, ^d Pulido-Villena et al. (2014a), ^e Wagener et al. (2010), ^f Wuttig et al. (2013), ^g T. Wagener et al., personal communication, 2011, ^h Desboeufs et al. (2014), ⁱ Bressac et al. (2014), nd: not determined.

(Table 2b) showed that changes in biomass were mostly due to an increase in phytoplankton biomass. POC_{dust} represented the major contribution of the POC pool over the 7 days of the experiments (POC_{dust} ~ 45–60 % of $\delta\text{POC}/\delta t$ for the three wet deposition simulations DUNE-P and DUNE-R, and 100 % for DUNE-Q following the nonstimulation of autotrophs by the dry deposition; Ridame et al., 2014).

Assuming that the budget is balanced, the dissolved organic carbon pool was estimated by the difference between the total organic carbon (Table 2a) and the particulate organic carbon pool (Table 2b). The partitioning between dissolved and particulate organic carbon was dominated by the dissolved pool with a DOC loss over 7 days of ~ 21 g C mesocosm⁻¹, or ~ 5 µmol CL⁻¹ d⁻¹ for the DUNE-P experiment, ~ 5 g C mesocosm⁻¹ or 1 µmol CL⁻¹ d⁻¹ for the DUNE-Q experiment, and a total of ~ 15 g C mesocosm⁻¹ or 3.5 µmol CL⁻¹ d⁻¹ for the DUNE-R experiment.

4 Discussion

4.1 Tested waters were low productive with low export, and heterotrophic

During all experiments, the tested waters were typical of oligotrophic conditions with low Chl *a* concentrations in the range 0.07–0.11 µg L⁻¹ (Table 1). Primary production measured over 7 years at the DYFAMED (DYnamique des Flux Atmosphériques en MEDiterranée) site in the Ligurian Sea in the surface mixed layer (SML) after the spring period ranged from 2 to 10 µg CL⁻¹ d⁻¹ (Marty and Chiverini, 2002), which is in good agreement with the PP rates measured in the tested waters during the DUNE ex-

periments (3.9–4.8 µg CL⁻¹ d⁻¹). Such values are typical of nonproductive waters of the open ocean (Del Giorgio et al., 1997). A recent review on heterotrophic bacteria in the Mediterranean Sea (Pulido-Villena et al., 2012) highlights the scarcity of data on bacterial respiration compared to abundance and production; only a few studies focus on the western basin, all showing high seasonal variability of BR for both coastal and open waters. BR values of the tested waters during the DUNE-Q (15 ± 3 µg CL⁻¹ d⁻¹) and DUNE-R (12 ± 2 µg CL⁻¹ d⁻¹) experiments were in the same range of the most recent data obtained in the SML at the open sea DYFAMED site (Pulido-Villena et al., 2008) with values in May being 14.4 ± 7.2 µg CL⁻¹ d⁻¹. The higher BR values during DUNE-P (35 ± 3 µg CL⁻¹ d⁻¹) are more similar to coastal data such as that reported by Navarro et al. (2004). As pointed out by these authors, the production of DOC by seagrass meadows, highly abundant in the DUNE study site, may be responsible for such high BR rates. The higher BR rates measured during DUNE-P compared to DUNE-Q and DUNE-R may be explained by the in situ conditions encountered during DUNE-P, typical of a late-spring post-bloom situation with lower seawater temperature, with smaller daily amplitude than during the other experiments.

Initial POC_{export} (2.4–9.8 mg C m⁻² d⁻¹) cannot be directly compared to any in situ data at the same depth (~ 15 m), as sediment traps usually placed below 100 m depth (see synthesis data for the Mediterranean Sea in Ternon et al., 2010). Comparing POC export in surface waters (15 m in the DUNE experiments) and at 150–200 m is difficult as a high remineralization occurs reducing rapidly the amount of POC as a function of water depth. Our numbers are representative of the POC export from the SML during summer in the western Mediterranean Sea (mixed layer depth from

Table 2a. Carbon mass budget. Data result from the integrated carbon fluxes over 7 days for DUST-MESO corrected from the integrated carbon fluxes over 7 days for the CONTROL-MESO. All data are in grams of C in the whole mesocosm. Budget of total organic carbon according to Eq. (2) in the text (Sect. 2).

In grams of C in the whole mesocosm	Estimated $\delta C_{org} / \delta t =$		(+) δPP	(+) $\delta_{estimated}$ DPP ^a	(−) δBR	(−) $\delta_{estimated}$ ZR ^b		(−) δPOC_{export}	(+) A_{tinput}
	min	max				min	max		
DUNE-P	−19.1	−19.3	1.7	1.0	−21.2	−0.2	−0.5	−0.48	0.128
DUNE-Q	−1.9	−2.0	0.13	0.08	−2.2	−0.02	−0.04	−0.05	0.128
DUNE-R	−6.9	−7.1	1.6	0.9	−9.1	−0.2	−0.4	−0.24	0.128
(1st seeding)									
DUNE-R	−6.1	−6.4	2.3	1.4	−9.4	−0.3	−0.6	−0.2	0.128
(2nd seeding)									

^{a,b} See Sect. 2.4.

Table 2b. Estimated induced changes in the particulate organic carbon pool inside the DUST mesocosms (see Sect. 2.4 for details).

Experiment	$\delta \text{POC} / \delta t =$	$+ \delta \text{Chl } a \text{ C}$ term	$+ \delta \text{zooplankton C}$ term		$+ \delta \text{bacteria C}$ term	$+ \text{POC}_{\text{dust}}$
			meso-	micro-		
DUNE-P	1.7	0.7	0.04	0	0.2	0.8
DUNE-Q	2.9	0	0	0	0	2.9
DUNE-R	0.9	0.35	0	0	0	0.5
(1st seeding)						
DUNE-R	1.3	0.55	0	0	0	0.7
(2nd seeding)						

Table 2c. Estimated induced changes in the dissolved organic carbon pool inside the DUST-MESO deduced from Tables 2a and 2b.

In grams of C in the whole mesocosm	$\delta C_{org} / \delta t$ (mean from Table 2a)	(+) $\delta POC / \delta t$ (from Table 2b)	($\delta DOC /$ δt)
DUNE-P	−19.2	1.7	−20.9
DUNE-Q	−1.9	2.9	−4.8
DUNE-R	−7.0	0.9	−7.9
(1st seeding)			
DUNE-R	−6.3	1.3	−7.6
(2nd seeding)			

10 to 15 m; D’Ortenzio et al., 2005). TERNON et al. (2010) measured an average daily POC flux at 200 m over 4 years of $11 \pm 12\text{ mg C m}^{-2}\text{ d}^{-1}$ at the DYFAMED site located in the northwestern Mediterranean Sea, with the lowest values from July to December. At the same site the daily average of the export in May–July at 200 m between 1988 and 2005 was $9 \pm 11\text{ mg C m}^{-2}\text{ d}^{-1}$ (Miquel et al., 2011). Our values at $\sim 15\text{ m}$ are in the lower range of those values for the Ligurian Sea at 200 m at the same period of the year, indicating that the POC export flux was extremely low in the tested waters during DUNE.

All those comparisons indicate that our study site is a low productivity oceanic system with low POC export. In the literature, the PP/BR ratio is commonly used to quantify the metabolic status of aquatic systems (see, for example, Del Giorgio et al., 1997). During DUNE, the average PP/BR ratio before seeding were always ≤ 0.5 (Fig. 1), indicating that the total organic carbon processed by bacteria exceeds by far the carbon fixed by phytoplankton: all the tested waters during DUNE before dust addition would thus be a source of dissolved CO_2 . This is in good agreement with findings that unproductive aquatic systems are net heterotrophic (Del Giorgio et al., 1997, Duarte et al., 2013). This was reported for the whole Mediterranean Sea (Duarte et al., 2013) and in the northwestern Mediterranean Sea in coastal (Bonilla-Findji et al., 2010) and open sea (Lemée et al., 2002).

4.2 A strong heterotrophic character remains after seeding

As argued in Guieu et al. (2014b), our large clean mesocosms are closed systems with no lateral advection, enclosing a body of water large enough to be representative of the water outside and where stocks and fluxes can be measured after a perturbation such as a simulated dust deposition. Here, we attempt to use the numbers obtained along with estimates

of unmeasured parameters in order to quantify how the carbon budget is affected after dust deposition.

As discussed in the introduction, most of the recent studies dealing with the impact of dust deposition on the surface ocean have focused on the stimulation of phytoplankton. A comprehensive study has been published recently indicating how the bacteria community can be stimulated preferentially to the autotroph community in the oligotrophic ocean (Marañón et al., 2010). These authors also show that this stimulation is likely a function of the degree of oligotrophy status where and when the dust deposition does occur. DUNE's results are in good agreement with this previous study as both bacteria activity and primary production have been stimulated by the wet dust input, the stimulation of the bacterial respiration being either higher than the net CO₂ fixation after the dust event (DUNE-R1 experiment) or equivalent (DUNE-P and DUNE-R2). The dust deposition did not produce a shift in the metabolic balance as the tested waters remained net heterotrophic. In the cases of DUNE-P and DUNE-Q experiments, the net heterotrophy was even enhanced by the dust deposition.

4.3 Stronger DOC consumption and POC export after wet deposition

The consequence of the dust addition was a strong DOC consumption inside the DUST-MESO: $\sim 5 \mu\text{mol CL}^{-1} \text{d}^{-1}$ for the DUNE-P experiment and a total of $3.5 \mu\text{mol CL}^{-1} \text{d}^{-1}$ for the DUNE-R experiment (DUNE-R1: $1.8 \mu\text{mol CL}^{-1} \text{d}^{-1}$; DUNE-R2: $1.7 \mu\text{mol CL}^{-1} \text{d}^{-1}$). The DOC consumption was lower ($\sim 1 \mu\text{mol CL}^{-1} \text{d}^{-1}$) for the DUNE-Q experiment. The same order of magnitude for DOC consumption found for DUNE-P and DUNE-R has been measured during heterotrophic phases at an oligotrophic, coastal Mediterranean site (Navarro et al., 2004), with a net DOC consumption as high as $18 \mu\text{mol CL}^{-1} \text{d}^{-1}$ and an average consumption during heterotrophic phases of $3.24 \pm 3.55 \mu\text{mol CL}^{-1} \text{d}^{-1}$. The authors of this last study indicated that such consumption implies that the system has to import DOC, either derived from land (storm runoff) or released by benthic communities. In our case, as our system does not allow allochthonous inputs, it means that our dissolved organic carbon stock inside the mesocosm should have decreased during the course of the experiment. Our DOC consumption over the whole mesocosm and over the 7 days following the seeding would have been 21, 5, 8, and 8 g C for DUNE-P, -Q, -R1 and -R2 experiments, respectively (Table 2c). This consumption has to be compared to the initial DOC concentration. DOC was measured only for DUNE-P and the average initial concentration was $87 \pm 9 \mu\text{M}$ ($n = 11$). This is comparable to the typical concentration of the oligotrophic situation at the open sea DYFAMED site for the same season ($75 \mu\text{M}$ – Pulido-Villena et al., 2008 – and $113 \mu\text{M}$ – Lemée et al., 2002) but lower than the maximum concentration measured

during a 16-month time series in a station overlying a *Posidonia oceanica* meadow at 8 m depth ($135 \mu\text{M}$, Bay of Blanes; Navarro et al., 2004). For DUNE-P, our DOC consumption likely indicates a decrease of $\sim 40\%$ of initial DOC stock inside the mesocosm after dust addition over 7 days, meaning a remaining DOC concentration at the end of the experiment of $52 \mu\text{mol CL}^{-1}$. In the absence of DOC measurement, if we assumed a comparable DOC initial concentration for DUNE-Q and DUNE-R, then our DOC consumption would indicate a decrease of $\sim 10\%$ (DUNE-Q) and a total decrease of $\sim 30\%$ (DUNE-R: R1+R2) of the DOC stock.

These numbers show that the strongest impact has been found for the simulated wet deposition (DUNE-P and DUNE-R) due to both a stronger stimulation of bacteria and phytoplankton activity and a stronger POC export. Indeed, in the case of simulated dry deposition (DUNE-Q), the autotrophs were not stimulated as the potential nitrogen or nitrogen/phosphorus ongoing colimitation of the phytoplanktonic activity could not be relieved (Ridame et al., 2014) and the dust addition allowed maintaining BR at its initial level whereas it was dramatically decreasing in CONTROL-MESO along the course of the experiment (Supplement Table S1). In addition, the ongoing stratification during DUNE-Q may have prevented in part the export of POC downward and as hypothesized by Desboeufs et al. (2014); the “lithogenic carbon pump” may have been inefficient due to initial organic matter inappropriate to induce a lithogenic ballasting in this experiment, whereas the fertilizing effect on phytoplankton associated to the experiments DUNE-P and DUNE-R was able to produce sufficient fresh organic matter to activate the lithogenic carbon pump (Bressac et al., 2014), leading to a total POC export out of the base of the mesocosms in 7 days of $\sim 0.5 \text{ g C}$ for DUNE-P and for DUNE-R (R1+R2) (Table 2a).

According to our estimates, the strong consumption of DOC following wet deposition for DUNE-P lead to a DOC final concentration 7 days after the event ($52 \mu\text{M}$) comparable to the minimum DOC surface concentrations found in winter in the Bay of Villefranche ($56 \mu\text{M}$; Bonilla-Findji et al., 2010) and in the surface waters at the open sea DYFAMED site in summer ($48 \mu\text{M}$, Lemée et al., 2002). However, as suggested by Pulido-Villena et al. (2014) after the second seeding of DUNE-R experiment, the viral lysis could have fed back in part the pool of DOC. Such mechanism could counterbalance in part the drawdown of DOC necessary to explain the important net consumption observed in DUNE-P and DUNE-R, in the absence of allochthonous input of DOC in our setup. Moreover, the extent of increase in bacterial respiration, and the still high bacterial respiration rates recorded during the second seeding in DUNE-R, when new phosphate was not consumed (Pulido-Villena et al., 2014), would also suggest an indirect effect by phytoplankton. Indeed, bacterial respiration could have been supported by fresh, labile phytoplankton-derived dissolved organic matter

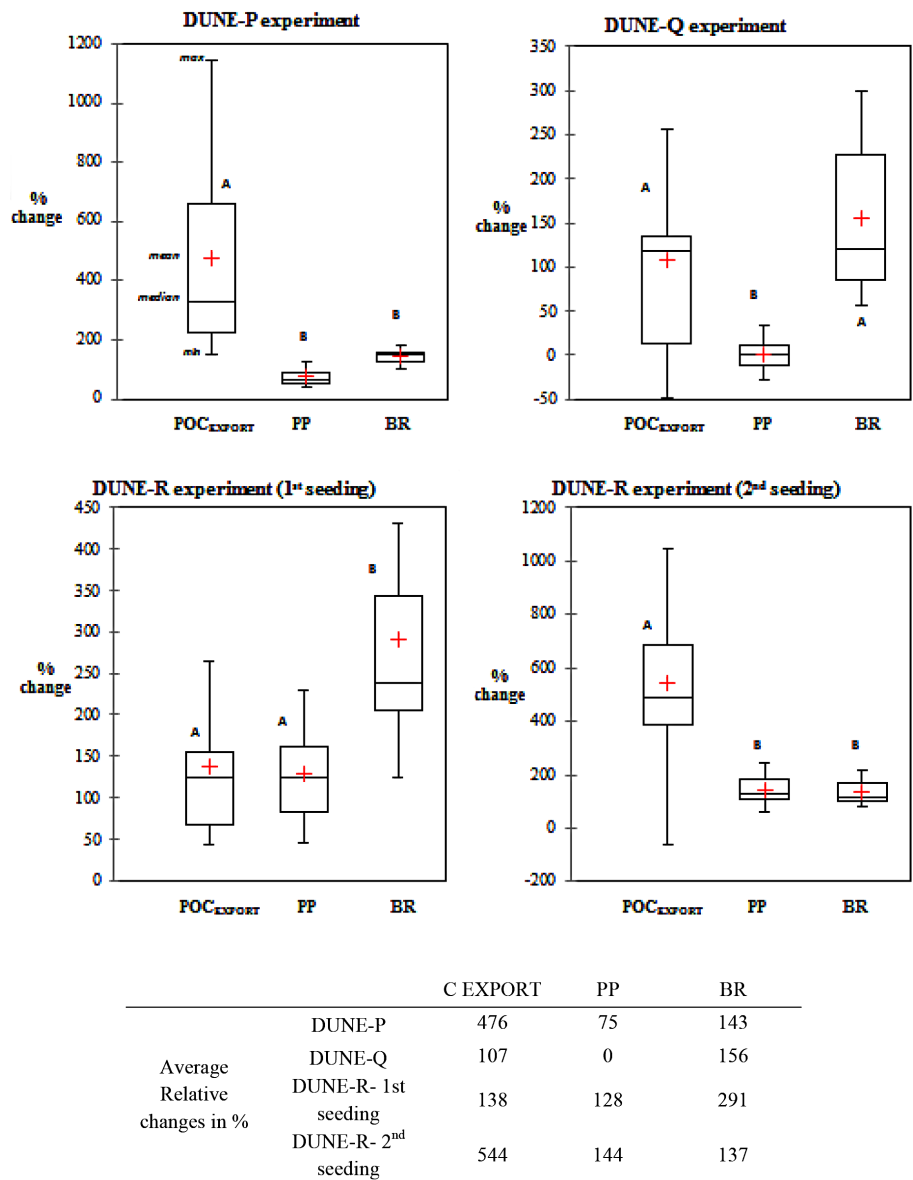


Figure 2. Box plots of the net fluxes expressed in relative change (%) and table with the average relative changes after the DUNE-P, -Q, -R1 and -R2 seedings, in percentage. The letters indicate the results of the statistical test in between the percentage of change for the POC_{EXPORT}, PP and BR. Means that were not significantly different between the different parameters ($p > 0.05$) were labeled with the same letter. The mean relative changes (RC, in %) = $(X_{\text{Dust}} - X_{\text{Control}}) \times 100 / (X_{\text{Control}})$ with X_{Control} is the mean for the three mesocosms CONTROL.

(DOM). Nevertheless, this tentative budget illustrates that in the absence of lateral advection from coastal sources or upwelling from deep waters, such heterotrophic system boosted by atmospheric wet deposition could decrease significantly the stock of dissolved organic carbon in the surface ocean, a question largely debated at the moment (see, for example, Duarte et al., 2013; Ducklow and Doney, 2013).

The net heterotrophy character of the tested waters remained (or even was increased) after the dust addition and the budget of total organic carbon was dominated by bacteria respiration resulting in a significant decrease of DOC stock

inside the mesocosm after a wet dust deposition was simulated. However, the system was still able to export POC. The DUNE data illustrate, thus, that a system can be dominated by heterotrophy and still maintain an export of particulate organic carbon even in the absence of allochthonous carbon inputs, on the short timescale concerned by the dust deposition event. This is different for open systems that can be heterotrophic while exporting organic carbon vertically only if allochthonous carbon inputs support both fluxes (Cole et al., 2007).

4.4 DUNE results in a broader context and further developments

DUNE is an important step forward in the way we understand dust deposition to the ocean in particular because the term “fertilization” is often associated with the a priori belief that dust deposition should increase chlorophyll biomass (despite some evidences of the contrary from satellite data; Dulac et al., 2004; Volpe et al., 2009) and carbon fixation (and thus increases atmospheric CO₂ drawdown). Instead, DUNE results have shown that by fertilizing predominantly heterotrophic bacteria, dust deposition in an oligotrophic environment induces the remineralization of DOC, thereby reducing atmospheric CO₂ drawdown (Rivkin and Anderson, 1997). As emphasized by Pulido-Villena et al. (2008, 2014), this may reduce substantially the fraction of the dissolved organic carbon stock in the surface ocean that can be exported to deep waters at the time of the winter mixing. Nevertheless, according to the “microbial carbon pump hypothesis” (Jiao et al., 2010), information on the lability of the remaining DOC pool after the enhanced bacterial respiration would be needed to better assess the net effect of dust deposition on DOC export.

DUNE has shown that the changes in carbon budget in oligotrophic environment are higher when the sea surface is impacted by a strong wet deposition rather than by a strong dry deposition. In the western Mediterranean region, mineral dust is mainly transported from the Sahara in the form of strong pulses (e.g., Loÿe-Pilot et al., 1986; Bergametti et al., 1989; Moulin et al., 1998; Guerzoni et al., 1999). According to Loÿe-Pilot and Martin (1996) from a 12-years time series of mineral dust deposition fluxes, the deposition is mainly (95 %) associated with wet deposition. The dominance of wet deposition was also shown in Ternon et al. (2010) over a 4-years time series of deposition (2003–2007). One development of this study would be to extrapolate our numbers to time series of deposition during similar oligotrophic conditions to evaluate the overall impact on the carbon budget at the event and seasonal scale in the surface waters of the northwestern Mediterranean Sea. Another interesting development of this study would be to predict possible scenario for the future using global biogeochemical models where dust pulses such as the ones simulated during DUNE are represented (Guieu et al., 2014a). Indeed, ongoing environmental changes (i.e., increasing temperature and stratification, expansion of the oligotrophic ocean, and changes in atmospheric deposition) could modify the role of atmospheric deposition on the biogeochemistry of low-nutrient, low-chlorophyll oceans such as the Mediterranean Sea. An adequate representation of the input of new atmospheric nutrients and particles in those models is timely (Guieu et al., 2014a). In particular, biogeochemical models should consider the important processes highlighted by the DUNE results such as bacterial respiration and (organic matter-dust)

aggregation, a process that allows particulate organic carbon export even in heterotrophic systems.

5 Conclusions

The DUNE project allows the first attempt to evaluate the changes induced in the carbon pools of an oligotrophic system after a simulated Saharan dust deposition above a large body of water during a 7-day period, while considering the vertical dimension. We show (i) that the organic carbon sinks dominate the organic carbon fluxes, demonstrating that the dust deposition induced a loss of organic carbon of the system in all the experiments, and (ii) that this loss is due to dissolved organic carbon consumption resulting in case of simulation of wet deposition in a significant drawdown of the DOC stock, that consequently will not be exported during the winter mixing. DUNE seeding experiments confirm that heterotrophic bacteria are key players in the response to dust deposition, as it was previously shown by Pulido-Villena et al. (2008) and Marañón et al. (2010) using microcosm approaches and Bonilla-Findji et al. (2010) from in situ data. Interestingly, we show that even dominated by heterotrophy, the closed system impacted by wet deposition still maintains a POC export out of the base of the mesocosms in 7 days of ~ 0.5 g C.

The Supplement related to this article is available online at doi:10.5194/bg-11-5621-2014-supplement.

Acknowledgements. The DUNE project, a DUST experiment in a low Nutrient, low chlorophyll Ecosystem, is a fundamental research project funded by the ANR under the contract ANR-07-BLAN-0126-01. It was conducted in partnership with the laboratory of LISA (Créteil), LEMAR (Brest), LOCEAN (Paris), and in collaboration with the laboratories LSCE (Gif-sur-Yvette), LOMIC (Banyuls), IRD/LOBP/COM (Marseille), CEFREM (Perpignan), CERES/ERTI, ENS (Paris) and the Regional Park of Corsica, Nature Reserve of Scandola. DUNE was also conducted in strong collaboration with the foreign research institute including the Institut des Régions Arides (IRA), Medenine (Tunisia), IFM-GEOMAR, Kiel (Germany), Stazione Zoologica Anton Dohrn, Naples (Italy) and the Alfred Wegener Institute, Bremerhaven (Germany). This work would not have been possible without the huge involvement of engineers F. Louis, J. M. Grisoni, and divers J. M. Grisoni, D. Luquet, M. C. Rouvières, and L. Gilleta from the Observatoire Océanologique de Villefranche-sur-Mer. We thank the RADEZOO service for the zooplankton analysis using the Zooscan system at the Observatoire Océanographique de Villefranche-sur-Mer (OOV). DUNE was endorsed by the international SOLAS (Surface Ocean – Lower Atmosphere Study) program in February 2009, (<http://solas-int.org/activities/project-endorsement.html>). The authors wish to thank Stephane Blain for many interesting and stimulating discussions and for his critical reading

of the manuscript. We thank CNRS-INSU and the Laboratoire d'Océanographie de Villefranche (LOV) for financing this publication. Finally, E. E. Garcia-Martin and two anonymous reviewers are acknowledged for their constructive and helpful comments.

Edited by: E. Marañón

References

- Alcaraz, M.: Summer zooplankton metabolism and its relation to primary production in the Western Mediterranean, *Oceanologica Acta*, Special Issue "Oceanographie Pelagique Mediterranee", edited by: Minas, H. J. and Nival, P., 185–191, 1988.
- Alcaraz, M., Calbet, A., Estrada, M., Marrasé, C., Saiz, E., and Trepát, I.: Physical control of zooplankton communities in the Catalan Sea, *Progr. Oceanogr.*, 74, 294–312, 2007.
- Aranguren-Gassis, M., Teira, E., Serret, P., Martínez-García, S., and Fernández, E.: Potential overestimation of bacterial respiration rates in oligotrophic plankton communities, *Mar. Ecol. Prog. Ser.*, 453, 1–10, 2012.
- Baines and Pace: The production of dissolved organic matter by phytoplankton and its importance to bacteria: Patterns across marine and freshwater systems, *Limnol. Oceanogr.*, 36, 1078–1090, 1991.
- Bergametti, G., Dutot, A. L., Buat-Ménard, P., Losno, R., and Remoudaki, E.: Seasonal variability of the elemental composition of atmospheric aerosol particles over the northwestern Mediterranean, *Tellus*, 41B, 353–361, 1989.
- Bonilla-Findji, O., Gattuso, J.-P., Pizay, M.-D., and Weinbauer, M. G.: Autotrophic and heterotrophic metabolism of microbial planktonic communities in an oligotrophic coastal marine ecosystem: seasonal dynamics and episodic events, *Biogeosciences*, 7, 3491–3503, doi:10.5194/bg-7-3491-2010, 2010.
- Bonnet, S., Guieu, C., Chiaverini, J., Ras, J., and Stock, A.: Effect of atmospheric nutrients on the autotrophic communities in a low nutrient, low chlorophyll system, *Limnol. Oceanogr.*, 50, 1810–1819, 2005.
- Bressac, M. and Guieu, C.: Post-depositional processes: What really happens to new atmospheric iron in the ocean surface?, *Global Biogeochem. Cy.*, 27, 859–870, 2013.
- Bressac, M., Guieu, C., Doxaran, D., Bourrin, F., Obolensky, G., and Grisoni, J. M.: A mesocosm experiment coupled with optical measurements to observe the fate and sinking of atmospheric particles in clear oligotrophic waters, *Geo-Mar. Lett.*, 32, 153–164, 2012.
- Bressac, M., Guieu, C., Doxaran, D., Bourrin, F., Desboeufs, K., Leblond, N., and Ridame, C.: Quantification of the lithogenic carbon pump following a simulated dust-deposition event in large mesocosms, *Biogeosciences*, 11, 1007–1020, doi:10.5194/bg-11-1007-2014, 2014.
- Calbet, A., Alcaraz, M., Saiz, E., Estrada, M., and Trepát, I.: Planktonic herbivorous food webs in the Catalan Sea (NW Mediterranean): temporal variability and comparison of indices of phyto-zooplankton coupling based on state variables and rate processes, *J. Plankt. Res.*, 18, 2329–2347, 1996.
- Cole, J. J., Prairie, Y. T., Caraco, N. F., McDowell, W. H., Tranvik, L. J., Striegl, R. G., Duarte, C. M., Kortelainen, P., Downing, J. A., and Middelburg, J. J.: Plumbing the Global Carbon Cycle: Integrating Inland Waters into the Terrestrial Carbon Budget, *Ecosystems*, 10, 172–185, 2007.
- de Leeuw, G., Guieu, C., Arneth, A., Bellouin, N., Bopp, L., Boyd, P., Denier van der Gon, H., Desboeufs, K., Dulac, F., Facchini, C., Gantt, B., Langmann, B., Mahowald, N., Marañón, E., O'Dowd, C., Olgun, N., Pulido-Villena, E., Rinaldi, M., Stephanou, E., and Wagener, T.: Ocean-Atmosphere interactions of particles, in: *Ocean-Atmosphere Interactions of Gases and Particles*, edited by: Liss, P. and Johnson, M., Springer Berlin Heidelberg, 171–246, 2013.
- Del Giorgio, P. A. and Cole, J. J.: Bacterial growth efficiency in natural aquatic systems, *Ann. Rev. Ecol. Systemat.*, 29, 503–541, 1998.
- Del Giorgio, P. A., Cole, J. J., and Cimbleris, A.: Respiration rates in bacteria exceed phytoplankton production in unproductive aquatic systems, *Nature*, 385, 148–151, 1997.
- Desboeufs, K., Leblond, N., Wagener, T., Nguyen, E. B., and Guieu, C.: Chemical fate and settling of mineral dust in surface seawater after atmospheric deposition observed from dust seeding experiments in large mesocosms, *Biogeosciences Discuss.*, 11, 4909–4947, doi:10.5194/bgd-11-4909-2014, 2014.
- D'Ortenzio, F., Iudicone, D., de Boyer Montegut, C., Testor, P., Antoine, D., Marullo, S., Santoleri, R., and Madec, G.: Seasonal variability of the mixed layer depth in the Mediterranean Sea as derived from in situ profiles, *Geophys. Res. Lett.*, 32, L12605, doi:10.1029/2005GL022463, 2005.
- Duarte, C. M., Regaudie-de-Gioux, A., Arrieta, J. M., Delgado-Huertas, A., and Agusti, S.: The Oligotrophic Ocean Is Heterotrophic, *Annu. Rev. Mar. Sci.*, 5, 551–69, 2013.
- Ducklow, H. W. and Doney, S. C.: What Is the Metabolic State of the Oligotrophic Ocean?, *A Debate*, *Annu. Rev. Mar. Sci.*, 5, 525–33, 2013.
- Dulac, F., Moulin, C., Planquette, H., Schulz, M., and Tartar, M.: African dust deposition and ocean colour in the eastern Mediterranean, in: *Proc. 37th CIESM Congress*, Barcelona, 7–11 June 2004, CIESM (Commission Internationale pour l'Exploration Scientifique de la Méditerranée), Monaco, p. 190, 2004.
- Fukuda, R., Ogawa, H., Nagata, T., and Koike, I.: Direct determination of carbon and nitrogen contents of natural bacterial assemblages in marine environments, *Appl. Environ. Microbiol.*, 64, 3352–3358, 1998.
- Giovagnetti, V., Brunet, C., Conversano, F., Tramontano, F., Obernosterer, I., Ridame, C., and Guieu, C.: Assessing the role of dust deposition on phytoplankton ecophysiology and succession in a low-nutrient low-chlorophyll ecosystem: a mesocosm experiment in the Mediterranean Sea, *Biogeosciences*, 10, 2973–2991, doi:10.5194/bg-10-2973-2013, 2013.
- Guerzoni, S., Chester, R., Dulac, F., Herut, B., Loje-Pilot, M. D., Measures, C., Migon, C., Molinaroli, E., Moulin, C., Rossini, P., Saydam, C., Soudine, A., Ziveri, and Ziveri, P.: The role of atmospheric deposition in the biogeochemistry of the Mediterranean Sea, *Progr. Oceanogr.*, 44, 147–190, 1999.
- Guieu, C., Dulac, F., Desboeufs, K., Wagener, T., Pulido-Villena, E., Grisoni, J.-M., Louis, F., Ridame, C., Blain, S., Brunet, C., Bon Nguyen, E., Tran, S., Labiadh, M., and Dominici, J.-M.: Large clean mesocosms and simulated dust deposition: a new methodology to investigate responses of marine oligotrophic

- ecosystems to atmospheric inputs, *Biogeosciences*, 7, 2765–2784, doi:10.5194/bg-7-2765-2010, 2010.
- Guieu, C., Aumont, O., Paytan, A., Bopp, L., Law, C. S., Mahowald, N., Achterberg, E. P., Marañoń, E., Salihoglu, B., Crise, A., Wagener, T., Herut, B., Desboeufs, K., Kanakidou, M., Olgun, N., Peters, F., Pulido-Villena, E., Tovar-Sanchez, A., and Völker, C.: The significance of the episodic nature of atmospheric deposition to Low Nutrient Low Chlorophyll regions, *Global Biogeochem. Cy.*, in revision, 2014a.
- Guieu, C., Dulac, F., Ridame, C., and Pondaven, P.: Introduction to the project DUNE, a DUst experiment in a low Nutrient, low chlorophyll Ecosystem, *Biogeosciences*, 11, 425–442, doi:10.5194/bg-11-425-2014, 2014b.
- Herut, B., Zohary, T., Krom, M. D., Mantoura, R. F. C., Pitta, P., Psarra, S., Rassoulzadegan, F., Tanaka, T., and Thingstad, T. F.: Response of East Mediterranean surface water to Saharan dust: on-board microcosm experiment and field observations, *Deep-Sea Res. II*, 52, 3024–3040, 2005.
- Jiao, N., Herndl, G. J., Hansell, D. A., Benner, R., Kattner, G., Wilhelm, S. W., Kirchman, D. L., Weinbauer, M. G., Luo, T., Chen, F., and Azam, F.: Microbial production of recalcitrant dissolved organic matter: long-term carbon storage in the global ocean, *Nat. Rev. Microbiol.*, 8, 593–599, 2010.
- Labasque, T., Chaumery, C., Aminot, A., and Kergoat, G.: Spectrophotometric Winkler determination of dissolved oxygen: re-examination of critical factors and reliability, *Mar. Chem.*, 88, 53–60, 2004.
- Lekunberri, I., Lefort, T., Romero, E., Vázquez-Domínguez, E., Romera-Castillo, C., Marrasé, C., and Gasol, J. M.: Effects of a dust deposition event on coastal marine microbial abundance and activity, bacterial community structure and ecosystem function, *J. Plankt. Res.*, 32, 381–396, 2010.
- Lemée, R., Rochelle-Newall, E., Van Wambeke, F., Pizay, M.-D., Rinaldi, P., and Gattuso, J.-P.: Seasonal variation of bacterial production, respiration and growth efficiency in the open NW Mediterranean Sea, *Aq. Microb. Ecol.*, 29, 227–237, 2002.
- López-Sandoval, D. C., Marañoń, E., Fernández, A., González, J., Gasol, J. M., Lekunberri, I., Varela, M., Calvo-Díaz, A., Morán, X. A. G., Álvarez-Salgado, X. A., and Francisco, G., and Figueiras, F. G.: Particulate and dissolved primary production by contrasting phytoplankton assemblages during mesocosm experiments in the Ría de Vigo (NW Spain), *J. Plankton Res.*, 32, 1231–1240, 2010.
- Loýe-Pilot, M.-D. and Martin, J. M.: Saharan dust input to the western Mediterranean: an eleven years record in Corsica, in: *The Impact of Desert Dust Across the Mediterranean*, edited by: Guerzoni, S. and Chester, R., Kluwer, 191–199, 1996.
- Loýe-Pilot, M.-D., Martin, J. M., and Morelli, J.: Influence of Saharan dust on the rain acidity and atmospheric input to the Mediterranean, *Nature*, 321, 427–428, 1986.
- Marañoń, E., Cermeño, P., and Pérez, V.: Continuity in the photo-synthetic production of dissolved organic carbon from eutrophic to oligotrophic waters, *Mar. Ecol. Prog. Ser.*, 299, 7–17, 2005.
- Marañoń, E., Fernández, A., Mouriño-Carballido, B., Martínez-García, S., Teira, E., Cermeño, P., Chouciño, P., Huete-Ortega, M., Fernández, E., Calvo-Díaz, A., Morán, X. A. G., Bode, A., Moreno-Ostos, E., Varela, M. M., Patey, D. M. D., and Achterberg, E. P.: Degree of oligotrophy controls the response of microbial plankton to Saharan dust, *Limnol. Oceanogr.*, 55, 2339–2352, 2010.
- Marty, J. C. and Chiaverini, J.: Seasonal and interannual variations in phytoplankton production at DYFAMED time-series station, north-western Mediterranean sea, *Deep-Sea Res. II*, 49, 2017–2030, 2002.
- Miquel, J. C., Martín, J., Gasser, B., Rodríguez-y-Baena, A., Toubal, T., and Fowler, S. W.: Dynamics of particle flux and carbon export in the northwestern Mediterranean Sea: A two decade time-series study at the DYFAMED site, *Progr. Oceanogr.*, 91, 461–481, 2011.
- Moulin, C., Lambert, C. E., Dayan, U., Masson, V., Ramonet, M., Bousquet, P., Legrand, M., Balkanski, Y. J., Guelle, W., Marticorena, B., Bergametti, G., and Dulac F.: Satellite climatology of African dust transport in the Mediterranean atmosphere, *J. Geophys. Res.*, 103, 13137–13144, 1998.
- Navarro, N., Agustí, S., and Duarte, C. M.: Plankton metabolism and dissolved organic carbon use in the Bay of Palma, NW Mediterranean Sea, *Aq. Microb. Ecol.*, 37, 47–54, 2004.
- Pérez, V., Fernández, E., Marañoń, E., Morán, X. A. G., and Zubkov, M. V.: Vertical distribution of phytoplankton biomass, production and growth in the Atlantic subtropical gyres, *Deep-Sea Res. Pt. I*, 53, 1616–1634, 2006.
- Pulido-Villena, E., Wagener, T., and Guieu, C.: Bacterial response to dust pulses in the western Mediterranean: Implications for carbon cycling in the oligotrophic ocean, *Global Biogeochem. Cy.*, 22, GB1020, doi:10.1029/2007GB003091, 2008.
- Pulido-Villena, E., Ghiglione, J.-F., Ortega-Retuerta, E., van Wambeke F., and Zohary, T.: Heterotrophic bacterian in the pelagic realm of the Mediterranean Sea, in: *Life in the Mediterranean Sea: a look at habitat changes*, Edited by: Stambler, N., Nova Science Publishers, Inc, 227–265, 2012.
- Pulido-Villena, E., Baudoux, A.-C., Obernosterer, I., Landa, M., Caparros, J., Catala, P., Georges, C., Harmand, J., and Guieu, C.: Microbial food web dynamics in response to a Saharan dust event: results from a mesocosm study in the oligotrophic Mediterranean Sea, *Biogeosciences Discuss.*, 11, 337–371, doi:10.5194/bgd-11-337-2014, 2014.
- Reinthal, T., Bakker, K., Manuela, R., Van Ooijen, J., and Herndl, G. J.: Fully automated spectrophotometric approach to determine oxygen concentrations in seawater via continuous-flow analysis, *Limnol. Oceanogr. Methods*, 4, 358–366, 2006.
- Ridame, C., Dekaezemacker, J., Guieu, C., Bonnet, S., and L'Helguen, S.: Phytoplanktonic response to contrasted Saharan dust deposition during mesocosm experiments, *Biogeosciences Discuss.*, 11, 753–796, 2014.
- Rivkin, R. B. and Anderson, M. R.: Inorganic nutrient limitation of oceanic bacterioplankton, *Limnol. Oceanogr.*, 42, 730–740, 1997.
- Tanaka, T. and Rassoulzadegan, F.: Full-depth profile (0–2000 m) of bacteria, heterotrophic nanoflagellates and ciliates in the NW Mediterranean Sea: Vertical partitioning of microbial trophic structures, *Deep-Sea Res. Pt. II*, 49, 2093–2107, 2002.
- Ternon, E., Guieu, C., Loye-Pilot, M.-D., Leblond, N., Bosc, E., Gasser, B., Miquel, J.-C., and Martin, J.: The impact of Saharan dust on the particulate export in the water column of the North Western Mediterranean Sea, *Biogeosciences*, 7, 809–826, doi:10.5194/bg-7-809-779 2010, 2010.

- Volpe, G., Banzon V. F., Evans R. H., Santoleri R., Mariano A. J., and Sciarra R.: Satellite observations of the impact of dust in a low-nutrient, low chlorophyll region: Fertilization or artifact?, *Global Biogeochem. Cy.*, 23, GB3007, doi:10.1029/2008GB003216, 2009.
- Wagener, T., Guieu, C., and Leblond, N.: Effects of dust deposition on iron cycle in the surface Mediterranean Sea: results from a mesocosm seeding experiment, *Biogeosciences*, 7, 3769–3781, doi:10.5194/bg-7-3769-2010, 2010.
- Williams, P. J. le B., Quay, P. D., Westberry, T. K., and Behrenfeld, M. J.: The Oligotrophic Ocean Is Autotrophic, *Annu. Rev. Mar. Sci.*, 5, 535–49, 2013.